

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 November 2002 (07.11.2002)

PCT

(10) International Publication Number
WO 02/088694 A2

(51) International Patent Classification⁷: **G01N 27/407**

(74) Agent: **GILL JENNINGS & EVERY**; Broadgate House,
7 Eldon Street, London EC2M 7LH (GB).

(21) International Application Number: **PCT/GB02/01984**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(22) International Filing Date: **1 May 2002 (01.05.2002)**

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

(25) Filing Language: **English**

(26) Publication Language: **English**

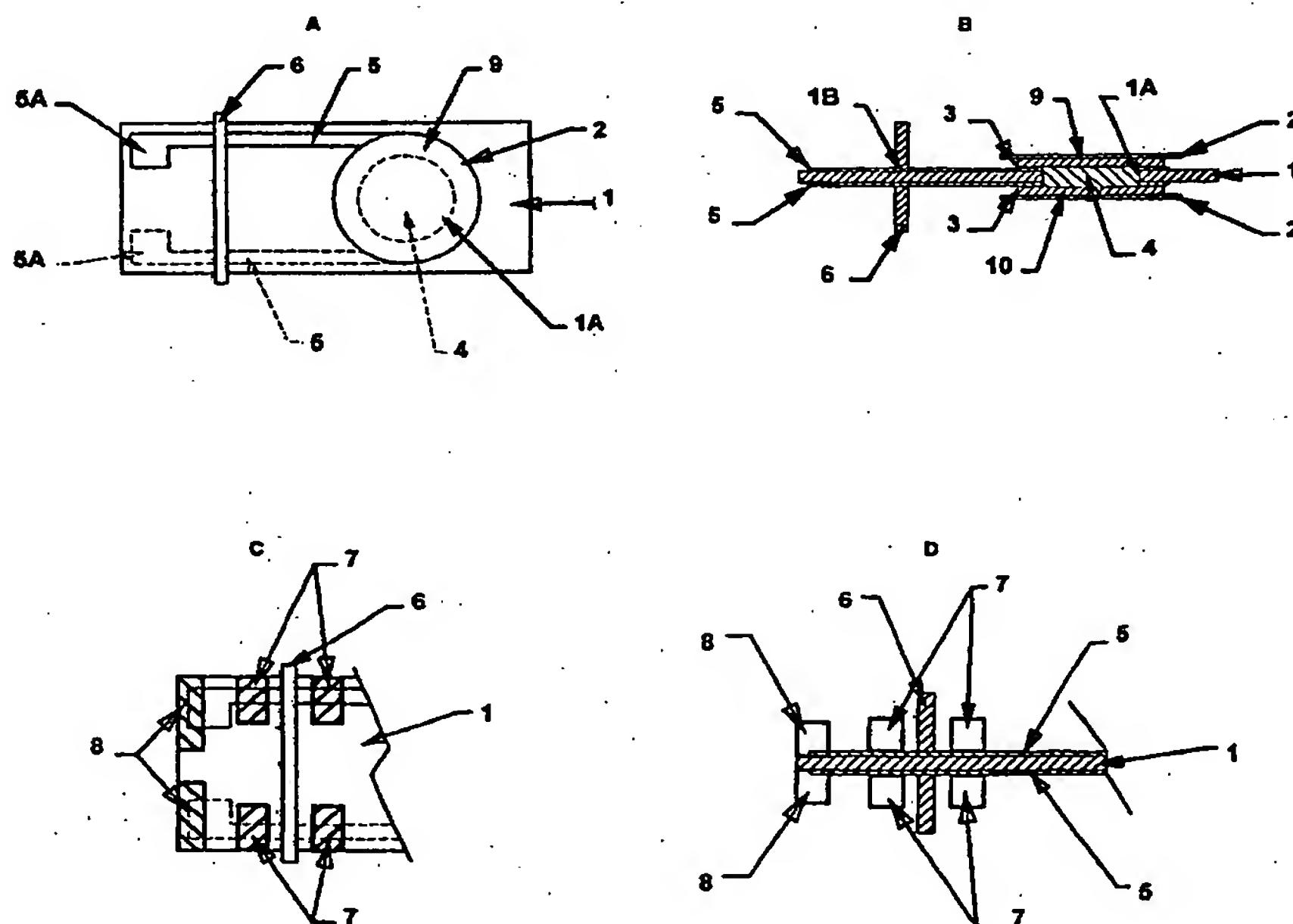
(30) Priority Data:
0110775.4 2 May 2001 (02.05.2001) GB

Published:

— without international search report and to be republished
upon receipt of that report

[Continued on next page]

(54) Title: ELECTROCHEMICAL GAS SENSOR



WO 02/088694 A2

(57) Abstract: An electrochemical gas sensor comprises sensing and counter electrodes (9, 10), current collectors (5) extending from each electrode, and a solid electrolyte (4) in contact with the electrodes, all supported on a common substrate (1) and located within a housing (6A) permitting gas access to the sensing electrode (9). The common substrate (1) projects from the housing to present portions of the current collectors for connection to other components.

WO 02/088694 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ELECTROCHEMICAL GAS SENSOR

The invention relates to electrochemical gas sensors of the kind comprising sensing and counter electrodes, current collectors extending from each electrode and an electrolyte in contact with the electrodes. Such sensors are hereinafter referred to as of the kind described.

Electrochemical gas sensors of the kind described are used for detecting a variety of gases including oxygen and toxic gases and an example is illustrated in GB-A-2094005. In these known examples, the electrodes are provided in a stack with electrolyte being transported into contact with the electrodes from a separate reservoir utilizing a wick. These known sensors suffer from a number of drawbacks, in particular the need to provide reservoir facilities for liquid and air and the need to transport liquid electrolyte to and from the reservoir in all orientations.

We have recently developed a new type of electrolyte material described in more detail in WO-A-02/11225 which is a solid polymer electrolyte. This overcomes a number of the problems mentioned above, in particular by eliminating the need for liquid electrolyte. In WO-A-02/11225, we illustrate the use of such a solid polymer electrolyte in a conventional stacked arrangement of electrodes.

Generally planar sensors using ionically conducting solid electrolytes are also known ("A CO₂ Sensor Based On A SC³⁺ Conducting Sc_{1.3}Zr₂(PO₄)₃ Solid Electrolyte", S Tamura, N Imanaka, M Kamikawa and G Adachi, Sensors & Actuators B 73 (2001) pp 205-210) while other proposals to overcome the drawbacks of liquid electrolytes have been described in "Extremely Stable Nafion Based Carbon Monoxide Sensor", P D van der Wal, N F de Rooij and M Koudelka-Hep, Sensors & Actuators B 35-36 (1996) pp 119-123.

In accordance with a first aspect of the present invention, an electrochemical gas sensor comprises sensing and counter electrodes, current collectors extending from each electrode, and a solid electrolyte in contact with the

electrodes, all supported on a common substrate and located within a housing permitting gas access to the sensing electrode, the common substrate projecting from the housing to present portions of the current collectors for connection to other components.

We have recognised for the first time that the use of a solid electrolyte not only enables the problems of liquid electrolyte to be overcome but enables new types of gas sensor to be developed in view of the ability to relax the requirements for liquid sealing and thus permit current collectors to extend through the housing. By providing these components on a common substrate which itself projects beyond the housing, a very rugged, highly compact and commercially viable sensor can be developed. The sensors are capable of operating over wide temperature and humidity ranges and offer long operating lifetimes of months or years with no connection to a liquid electrolyte reservoir.

Furthermore, the ability to employ planar designs rather than stacks offers greater compatibility with automated assembly. The reduced demands placed upon the housing sealing allows simple mechanical closure methods to be employed in place of thermal or ultrasonic welding, both of which may have undesirable effects upon the internal structure of sensors.

Thus, in accordance with a second aspect of the present invention, a method of constructing an electrochemical gas sensor comprises providing sensing and counter electrodes, current collectors extending from each electrode, and a solid electrolyte in contact with the electrodes, all supported on a common substrate and located within a housing permitting gas access to the sensing electrode, the common substrate projecting from the housing to present portions of the current collectors for connection to other components.

In some cases, the common substrate will project through an aperture in the housing wall but in others, the common substrate can form part of the housing itself. This latter arrangement is a particularly advantageous feature
5 of the invention.

The electrodes can be positioned on opposite sides of the substrate with the solid electrolyte between them but more conveniently, the electrodes are provided on the same side of the substrate. This leads to ease of manufacture.
10

The invention is applicable to both two and three electrode sensors, a reference electrode being provided in the case of a three electrode sensor and indeed can be extended to multiple sensing electrodes. In general, where
15 a reference electrode is used, this will be isolated from the gas to be sensed. However, in some forms of reference sensor (for example, Ir/IrO₂ couples) this constraint can be relaxed.

The electrodes could be provided by conventional electrocatalyst supported on carriers such as PTFE tapes
20 but in preferred examples, the electrodes are deposited on the solid electrolyte. This again leads to a more simplified method of construction and a reduction in component numbers.

Preferably, the common substrate has a one piece construction although laminate structures are also envisaged.
25

As mentioned above, the electrodes could be provided on opposite sides of the substrate and a particularly convenient way of achieving this is by forming a substrate as a folded member, the electrodes being provided on the same side of the folded member when in its unfolded condition. Again, this leads to simplification in manufacture. The substrate could also be folded the other way so that the electrodes and electrolyte are provided
30
35 between the folds.

The common substrate can be made from any convenient, electrically insulating material. Examples include polyimide, polyester, FR4, and injection moulded plastic.

The solid electrolyte will be chosen according to the conditions under which the sensor will be used. A variety of solid polymer electrolytes could be used, such as Nafion, but the preferred electrolyte comprises a fluorinated polymer matrix and a charge carrying component which is dispersed and immobilised in the matrix, the charge carrying component consisting of a fluorinated organic proton conductor which is chemically compatible with the polymer. Such solid polymer electrolytes are described in more detail in WO-A-02/11225.

The absence of liquid electrolyte together with the provision of the current collectors on the common substrate allows electronic or "smart" components to be mounted on the common substrate and electrically connected with the current collectors. This can be achieved both inside and, particularly advantageously, outside the housing.

The incorporation of electronic components can be envisaged at a number of levels varying from simple set on test components to the incorporation of all instrument functions on the common substrate. This might additionally require the provision of extra tracks to bring power into the sensor from an external supply to power such circuits. Alternatively, an integrated mounting battery connector, or printed battery or fuel cell technologies can be used. A unitary component of this type could also be used to mount the control electronics (e.g. potentiostatic circuits, electrode biasing means or the like) required by some designs of electrochemical sensor. The passive or active hardware components (and any associated software) might be positioned in a number of locations between the electrode and the "instrument" termination.

The components can include:

- simple trimming resistor or other set-on-test component

- passive, memory-only EEPROM containing electronic data sheet, for example as envisaged in the IEEE1451 standard or some sub-set of such information. Could be a combination of read-only (i.e. manufacturers written data) and read/write (i.e. in-use calibration) results
- analogue-digital conversion and/or head amplification for improved signal transmission characteristics (noise suppression)
- active processor-based system performing real time compensation or correction e.g. based on local temperature measurement (a/d is probably a desirable precursor in any realistic system). This could be seen as effectively integrating the instrument electronics into the sensor itself
- addition of a display, indicator, alarm or other audio-visual output device to the above.

By a suitable choice of components, a self-contained gas sensing instrument can be constructed which includes electronic components on the common substrate for processing signals from the electrodes to determine gas concentration and a display for displaying gas concentration. In this case, no additional electronic components are required except a power supply unless this also is provided on the common substrate.

Due to the compact nature of the gas sensors, a further aspect of the invention is the provision of a gas sensing assembly comprising a sensor according to the invention; and a support to which the gas sensor can be removably attached, the support defining a plenum chamber. Thus, the gas sensor can be easily replaced at the end of its life.

In some applications, there is a need to be able to sense for different gases and thus the support may define more than one plenum chamber to each of which a gas sensor

can be removably attached. Each gas sensor will then be chosen in accordance with the gas to be sensed. In this case, each plenum chamber may include respective, different formations which cooperate with corresponding formations on 5 respective sensors of different types so that only one type of sensor can be attached to each plenum chamber.

The electrodes may have a conventional construction comprising a mixture of electrocatalyst and hydrophobic material forming gas channels and so creating a gas permeable electrode structure. Alternatively, one or more 10 of the electrodes may not be gas permeable but comprise a solid film of electrocatalyst, the three phase interface being formed at the junction of the solid electrolyte, the gas phase and the catalyst.

15 The current collectors can also comprise conventional components such as flattened ribbons of precious metal, for example platinum, or conducting polymer, as appropriate to the substrate type selected (e.g. screen printed precious metal conductors on a conventional solid or flexible pcb, 20 or embossed plated elements on a plastic strip). The invention allows the current collectors to be easily provided, for example by screen printing. Other methods include embossing and hot foiling.

Typically, the housing provides a gas access control 25 aperture such as a gas phase diffusion barrier or the like. Thus, the sensor housing can fulfil multiple roles of physical support for electrodes/ electrolyte, control of gas access (via "traditional" diffusion barrier options) and current collection, so allowing further reductions in 30 component count and manufacturing complexity.

Some examples of gas sensors according to the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1A is a plan of part of a two electrode sensor;
35 Figure 1B is a cross-section through the sensor part shown in Figure 1A;

Figure 1C is a partial plan of the Figure 1A example showing a number of smart components;

Figure 1D is a cross-section through the partial plan of Figure 1C;

5 Figures 2A and 2B are views similar to Figures 1A and 1B but of a second example of the two electrode sensor;

Figures 3A and 3B are views similar to Figures 1A and 1B but of a further example of the two electrode sensor and illustrating the complete housing;

10 Figures 4A and 4B are views similar to Figures 3A and 3B but illustrating a three electrode sensor;

Figure 5A is a plan of another example of a three electrode sensor;

15 Figures 5B and 5C are sections on the lines A-A and B-B respectively in Figure 5A;

Figure 6 illustrates a plenum chamber;

Figure 7 illustrates a sensor being inserted into the plenum chamber of Figure 6;

20 Figure 8 illustrates three plenum chambers in series; and,

Figures 9A and 9B are a plan and cross-section respectively of an entire gas sensing instrument.

In the examples to be described, those components which are the same are given the same reference numbers.

25 Figures 1A and 1B illustrate the gas sensing components of a two electrode gas sensor. This comprises a single piece substrate 1 formed of polyimide or equivalent material and having an aperture 1A in which is secured by pressure bonding a block of solid polymer electrolyte (SPE) 4. A pair of current collectors 5 of for example platinum are screen printed onto opposite surfaces of the substrate 1 and contact the SPE 4 which stands proud of the major surfaces of the substrate 1. The current collectors 5 terminate in respective integral pads 5A.

30 On top of the substrate 1 and SPE 4 is provided a sensing electrode 9 comprising an electrocatalyst (for example PTFE/Pt mixture or similar) 3 supported on a

backing tape (for example PTFE or similar) 2. A counter electrode 10 of similar construction is provided on the underside of the substrate 1, both electrocatalysts 3 being in contact with the SPE 4 and respective current collectors 5. The SPE 4 can be adequately secured to the electrocatalyst layers 3 for assembly purposes by applying a small amount of pressure and then releasing. The SPG material is naturally 'tacky' and so is effectively self adhesive (although can be peeled off from some surfaces with care). In practise, the outer housing will provide some compression and retention of the assembly in long term use. It should be noted that the catalyst actually has greater affinity for the SPE than for the PTFE tapes and retaining adequate contact has not been a major problem.

The sensing and counter electrodes 9,10 are located within an outer housing of which part of one wall 6 is shown in Figures 1A and 1B. This outer housing will include a gas controlling access aperture such as a gas phase, knudsen or solid diffusion barrier to control the access of gas to the sensing electrode 9. Oxygen access to the counter electrode is provided by the same means (not shown) as those well known in the design of electrochemical gas sensors based on wet electrolytes. It is common practise to provide a very small leak path through the sensor casing to the counter, which is highly restrictive in comparison with the controlled gas diffusion access to the sensing electrode region. (This high restriction derives from the much greater partial pressure of oxygen in the atmosphere as compared with the target gas).

Alternatively, a porous section can be incorporated in the casing (eg a solid diffusion membrane) to allow a controlled amount of gas to reach the counter. The requirement for oxygen access depends on the demands placed on the counter, and in some cases (low concentration sensors), the oxygen reservoir within the porous backing tape might satisfy short term requirements without any

additional measures. The key point is that there will be no overt efforts to hermetically seal the counter.

The substrate 1 extends through an aperture 1B in the wall 6 so that the pads 5A are located externally of the wall for connection to other instrumentation. It should be understood that although the Figures show current tracks 5 passing through the sensor wall 6 on both sides of the substrate 1, conventional techniques such as through-hole plating could be used to bring both tracks onto one side of the substrate in the area remote from the electrodes. Other embodiments are also envisaged, for example where the current collectors are formed as one or more internal layers of the substrate, much as in a multi-layer pcb, and are only brought to the surface where connection to the electrode is required. This might be advantageous if, for example, one wished to use a metal sensor housing which could otherwise short these connections.

In this example, the electrocatalyst is shown as being backed by PTFE tape, as in conventional liquid electrolyte cells. In all subsequent examples, however, the catalyst is depicted as having been deposited directly on to the SPE material itself. Where the properties of the relevant materials allow the latter method to be employed, it is to be favoured due to the simplification of assembly processes and reduction in part count.

Although the pads 5A could be connected to remote instrumentation, as explained above, an important aspect of the invention is that electronic components can be mounted on the substrate 1. This is illustrated in Figures 1C and 1D where a number of "smart" components 7 are mounted on the substrate 1 in electrical communication with the tracks 5 and on either side of the wall 6 while further output connectors 8 are mounted in electrical connection with the pads 5A. Examples of the connectors 8 which might be attached to the pads are solderable pins, pcb edge connectors, sprung pressure contacts, in-line headers, flexible circuit 'tails' and other well known standard

electronic types. It should also be understood that extensions of the current collectors to the right of the electrode/SPE area in Figures 1C and 1D could offer other equally suitable locations. The Figures do not show additional conductive tracks which might be required to bring power and/or input/output data lines to the smart components, but these are fundamentally similar to those required for current collection purposes.

The smart components are illustrated here as sitting on continuous current collectors, but in some or all cases the current collectors may be "discontinuous" in that the component circuitry "interrupts" the link, as shown in Figure 9. (There might be a switch to allow intermittent measurements, for example.)

Figures 2A and 2B illustrate a sensor substantially the same as that shown in Figures 1A and 1B except that the substrate 1 has been folded at 1C. The folded leaves may be internally bonded together or could be held together under pressure from the external housing. Suitable materials which can be folded include any materials typically used for flexible printed circuit fabrication. For example, polyester, polyimide and Kapton are well known in such applications. It should also be noted that the tracking applied to such substrates must be equally flexible to avoid cracking on folding. Annealed copper is commonly used in such applications. The primary advantage of this is that the conductive tracks 5 can be printed on one side of the substrate 1 only, while in its unfolded condition. The substrate is then folded as shown in Figure 2B and the SPE 4 and sensing and counter electrodes 9,10 then added. It will be noted in Figure 2B that in this case the sensing and counter electrodes are shown as a single layer of electrocatalyst 3 which has been deposited on the SPE 4.

Figures 3A and 3B illustrate a further example of a two electrode sensor in which the current collectors 5 are provided on the same side of the substrate 1. Furthermore,

the full cross-section of the housing 6A is shown although it will be noted that the substrate 1 together with the current collectors 5 still project through an aperture 1B in the wall part 6. The housing 6A has a gas phase diffusion barrier 12 formed by a small opening which is in communication with the sensing electrode 9 and a dividing wall 6B. The wall 6B serves to restrict gas flow to the counter electrode 10 so as to substantially prevent gas to be sensed reaching the counter electrode but instead to react at the sensing electrode 9.

As far as oxygen access to the counterelectrode 10 is concerned, the sensor output may be considered as representing the differential effect of the ambient species upon the sensing and counter electrodes. Thus, it is generally considered good practise to limit the exposure of the counter to the ambient in order to maximise the output. For an oxygen reduction counter in trace toxic gas sensors of the type considered here, oxygen is present at far higher concentrations than the target species. Therefore, the counter can be kept fully supplied via a leak path (not shown) through the casing which is far more restrictive than the diffusion controlled gas access to the sensing electrode. Any target gas which does access via this route has negligible effect upon the overall cell behaviour. It is well known from the art in designing gas sensors using wet electrolytes that leakage paths are easily built into the outer sensor housing to achieve this aim. Alternatively, low permeability solid membranes might also be used to provide a controlled access to the counter.

It is also worth noting that if the counter electrode 10 was provided on a porous PTFE backing tape then the tape will itself act as a significant oxygen reservoir. However, with no backing tape (as shown), the counter electrode will be porous, particularly if made of PTFE/Pt black or even just Pt black. Depending upon the current demands made on the counter, this may obviate the need for any additional access route, although it would generally be

considered good design practise to provide for the more extreme circumstances where one might be needed.

It will be apparent that hermetic sealing of the counter from the remaining electrodes is not usually part of the design philosophy. However, there are some circumstances in which additional precautions are required. If the counter reaction is one which could produce species capable of reacting at the sensing (eg in the case of hydrogen evolution in a CO sensor) additional precautions may be prudent or indeed essential. More pertinently (and as considered further below) many reference systems are prone to drift in the presence of reactive species and so gas path management becomes more important in this context.

Figures 4A and 4B illustrate a structure similar to that shown in Figures 3A and 3B but for a three electrode sensor, an additional reference electrode 11 being provided. In this case, the reference electrode 11 is isolated from the ambient by the wall 6B due to the undesirable effects of CO on a Pt/air reference system. This is because such references can be dramatically affected by the presence of reactive species (like CO), although other reference systems do not rely on the presence of air (oxygen) and so are far less prone to such problems. It follows that, since any reactive species is likely to upset the reference potential, the greater its isolation from the ambient atmosphere, the more stable its potential is likely to be. However, alternative forms of reference system, for example utilizing Ir/IrO₂ couples, would allow this constraint to be relaxed.

Figures 5A-5C illustrate another example of the three electrode sensor utilizing a folded substrate 1. This differs from previous examples in that the components are located between the folds of the substrate 1 while the substrate 1 forms part of the sensor housing. Thus, as can be seen in the drawings, the substrate 1 is folded into a U-shaped form (Figures 5B and 5C) and is secured behind flanges 6C of the housing 6A so that the lower fold of the

substrate 1 effectively forms part of the housing. The sensing and counter electrodes 9,10 are formed on opposite sides of the SPE 4 and are substantially coterminous, in the form of discs. The reference electrode 11 has a part 5 annular, horseshoe configuration, is located radially outwardly of the sensing and counter electrodes 9,10, and is coplanar with the counter electrode 10. We have found that in the case of this "stacked" configuration, it is important that the sensing electrode footprint does not, or 10 does not significantly, overlap the footprint of the reference electrode. This is achieved by the configuration shown in Figure 5.

It will be noted in Figures 5B and 5C that there appear to be gaps between the electrodes and the substrate 15 but in practice, these gaps will be closed once the sensor has been fully assembled and is held under pressure. The compression of the electrode / electrolyte assemblies shown in the various diagrams is achieved by squeezing the components together during the closure process. Compression ribs (not shown) may be provided at appropriate points on the inside of the housing to create regions of greater compression within the assembly as demanded by the details of the design. The outer casing will be attached by well known means such as ultrasonic welding or heat sealing. 20 This aspect of the SPE sensor design may be considered as crudely analogous to the stack compression provided in traditional wet electrolyte systems. However, the constraints in wet systems are obviously much greater due 25 to the need to prevent liquid leakage.

Each current collector 5 is screen printed on the internal surface of the substrate 1 and is coupled via a respective through-hole 13 with a corresponding pad 5A. 30

It will also be noted that a large aperture 20 is provided in the upper fold of the substrate 1 to allow gas 35 to reach the sensing electrode 9. This aperture 20 is not gas controlling.

An hermetic seal is formed between the substrate 1 and the upper portion of the housing 6A and this can readily be achieved with appropriate choice of materials and sealing techniques, since the demands upon such a seal are greatly relaxed in the absence of aggressive liquid electrolyte.

It should be noted that the sensor designs depicted in the drawings could also be extended to include a number of sensing electrodes sharing the same SPE 4 and counter/reference electrodes 9,10. The only modification required to achieve this would be the splitting of sensing electrode 9 into a number of isolated sections, each provided with its own current collector 5.

Having now described a number of different gas sensor constructions, we will now consider a number of ways in which these gas sensors can be incorporated into a larger instrument.

Figure 6 illustrates in schematic cross-section a gas plenum chamber 14 having a gas inlet 15 and a gas outlet 15' through which gas can flow and a further inlet aperture 15A allowing gas to flow into a receptacle 21. The receptacle 21 is constructed such that a gas sensor of the type shown previously (Figure 5) can be slid into the receptacle 21 to bring the pads 5A into electrical contact with electrical connectors 16 mounted to the receptacle 21. This is shown in Figure 7. The sensor might be a simple push fit, but there could also be a simple flexing element to provide a locking function. Alternatively, a "heel and toe" snap fit arrangement could be employed to locate and retain the sensor. The connectors 16 are preferably spring loaded contacts mating with the pads 5A, but many other variants are known and would be equally suitable.

Figure 8 illustrates an extension of the arrangement shown in Figure 6 in which a number of gas plenums 14 and associated receptacles 21 are fitted together in series, with the gas outlet 15' of one plenum communicating with the gas inlet 15 of the next. These could have an identical form but in this example each receptacle 21 has

a slightly different form. By forming gas sensors associated with different gases with correspondingly different shapes, only a gas sensor of a particular form can be located in each receptacle and thus the gas being sensed by the sensor in each receptacle will be known.

As will be appreciated from Figure 8, an important aspect of this is that in a three sensor system, only four parts are required (an integral housing assembly as shown in Figure 8 and three gas sensors).

10. It will also be appreciated in Figures 6, 7 and 8 that although an envelope/post slot concept is shown, other options are possible. For example, the example might be turned through 90° so that sensors are posted in from above (or below).

As has been mentioned previously, it is possible to mount one or more smart, electronic components on the common substrate both internally and externally of the housing. Figures 9A and 9B are intended to illustrate an entire gas sensing instrument fabricated on the same substrate 1. The smart components 7 in this case would go well beyond what would normally be considered as forming part of the sensor. Thus, there can be a display, and user interface means (for example a touch sensitive switch for function selection and powering). A battery supply might also be incorporated within this enclosure. The distinction from current practice (where the sensor would usually be in a separate self-contained housing, allowing it to be mounted onto and removed from the instrument), is that the sensor is itself built onto the common substrate, either before or after the remainder of the instrument has been manufactured.

CLAIMS

1. An electrochemical gas sensor comprising sensing and counter electrodes, current collectors extending from each electrode, and a solid electrolyte in contact with the electrodes, all supported on a common substrate and located within a housing permitting gas access to the sensing electrode, the common substrate projecting from the housing to present portions of the current collectors for connection to other components.
10
2. A sensor according to claim 1, wherein the common substrate projects through an aperture in the housing.
3. A sensor according to claim 1, wherein the common substrate forms part of the housing.
- 15 4. A sensor according to claim 1 or claim 2, wherein the electrodes are positioned on opposite sides of the substrate with the solid electrolyte between them.
5. A sensor according to any of claims 1 to 3, wherein the electrodes are provided on the same side of the substrate.
20
6. A sensor according to any of the preceding claims, further comprising a reference electrode and a respective current collector contacting the reference electrode, the electrode and current collector being provided on the common substrate and the reference electrode contacting the solid electrolyte.
25
7. A sensor according to claim 6, wherein the reference electrode is isolated from a gas to be sensed by part of the housing.
- 30 8. A sensor according to any of the preceding claims, further comprising more than one sensing electrode and associated current collector, the sensing electrodes being isolated from each other with respect to gas access but sharing the same counter electrode, and reference electrode if provided.
35

9. A sensor according to any of the preceding claims, wherein the electrodes are supported on carriers such as PTFE tapes.
10. A sensor according to any of claims 1 to 8, wherein the electrodes are deposited on the solid electrolyte.
11. A sensor according to any of the preceding claims, wherein the substrate has a one piece construction.
12. A sensor according to any of the preceding claims, wherein the substrate comprises a folded member, the electrodes being provided on the same side of the folded member when in its unfolded condition.
13. A sensor according to claim 12, wherein the electrodes and solid electrolyte are positioned between the folds of the folded member.
14. A sensor according to any of the preceding claims, wherein the common substrate comprises one of polyimide, polyester, FR4, and injection moulded plastic.
15. A sensor according to any of the preceding claims, wherein the solid electrolyte comprises a solid polymer electrolyte.
16. A sensor according to claim 15, wherein the solid polymer electrolyte comprises a fluorinated polymer matrix and a charge carrying component which is dispersed and immobilised in the matrix, the charge carrying component consisting of a fluorinated organic proton conductor which is chemically compatible with the polymer.
17. A sensor according to any of the preceding claims, wherein the common substrate supports at least one electronic component in electrical contact with one or more of the current collectors.
18. A sensor according to claim 17, wherein the electronic component is located outside the housing.
19. A sensor according to claim 17 or claim 18, wherein the electronic component comprises a thermistor, potentiostatic circuit, EEPROM, display, user interface, power supply, or microprocessor.

20. A gas sensor according to claim 19, the sensor including electronic components on the common substrate for processing signals from the electrodes to determine gas concentration and a display for displaying gas concentration.
- 5
21. A sensor according to any of the preceding claims, wherein the housing includes a gas access aperture for controlling the access of gas to the sensing electrode.
22. An assembly according to claim 21, wherein the gas access aperture comprises a gas phase, knudsen or solid membrane diffusion barrier.
- 10
23. A gas sensing assembly comprising a gas sensor according to any of the preceding claims; and a support to which the gas sensor can be removably attached, the support defining a plenum chamber.
- 15
24. An assembly according to claim 23, wherein the support defines more than one plenum chamber to each of which a gas sensor can be removably attached.
25. An assembly according to claim 24, wherein each plenum chamber includes respective, different formations which cooperate with corresponding formations on respective sensors of different types so that only one type of sensor can be attached to each plenum chamber.
- 20
26. An assembly according to claim 24 or claim 25, wherein the plenum chambers are connected in series such that gas can pass from one to the other.
- 25
27. An assembly according to any of claims 21 to 26, wherein the or each gas sensor is slidably mounted to the support.
- 30
28. An assembly according to any of claims 21 to 27, further comprising a locking system for releasably locking the or each gas sensor to the support.
- 35
29. A method of constructing an electrochemical gas sensor, the method comprising providing sensing and counter electrodes, current collectors extending from each electrode, and a solid electrolyte in contact with the electrodes, all supported on a common substrate and located

within a housing permitting gas access to the sensing electrode, the common substrate projecting from the housing to present portions of the current collectors for connection to other components.

- 5 30. A method according to claim 29, wherein the sensing
and counter electrodes, solid electrolyte and current
collectors are provided on the same side of the common
substrate.

10 31. A method according to claim 30, further comprising
folding the common substrate so as to bring portions of the
other side of the substrate substantially into contact with
one another whereby the electrodes are positioned facing
away from each other.

15 32. A method according to any of claims 29 to 31, wherein
the electrodes are deposited, for example printed, on the
solid electrolyte.

20 33. A method according to any of claims 29 to 32, wherein
the common substrate is held under pressure against the
housing wall.

25 34. A method according to any of claims 29 to 33, further
comprising securing one or more electronic components to
the current collectors.

30. A method according to any of claims 29 to 34 for
constructing a gas sensor according to any of claims 1 to

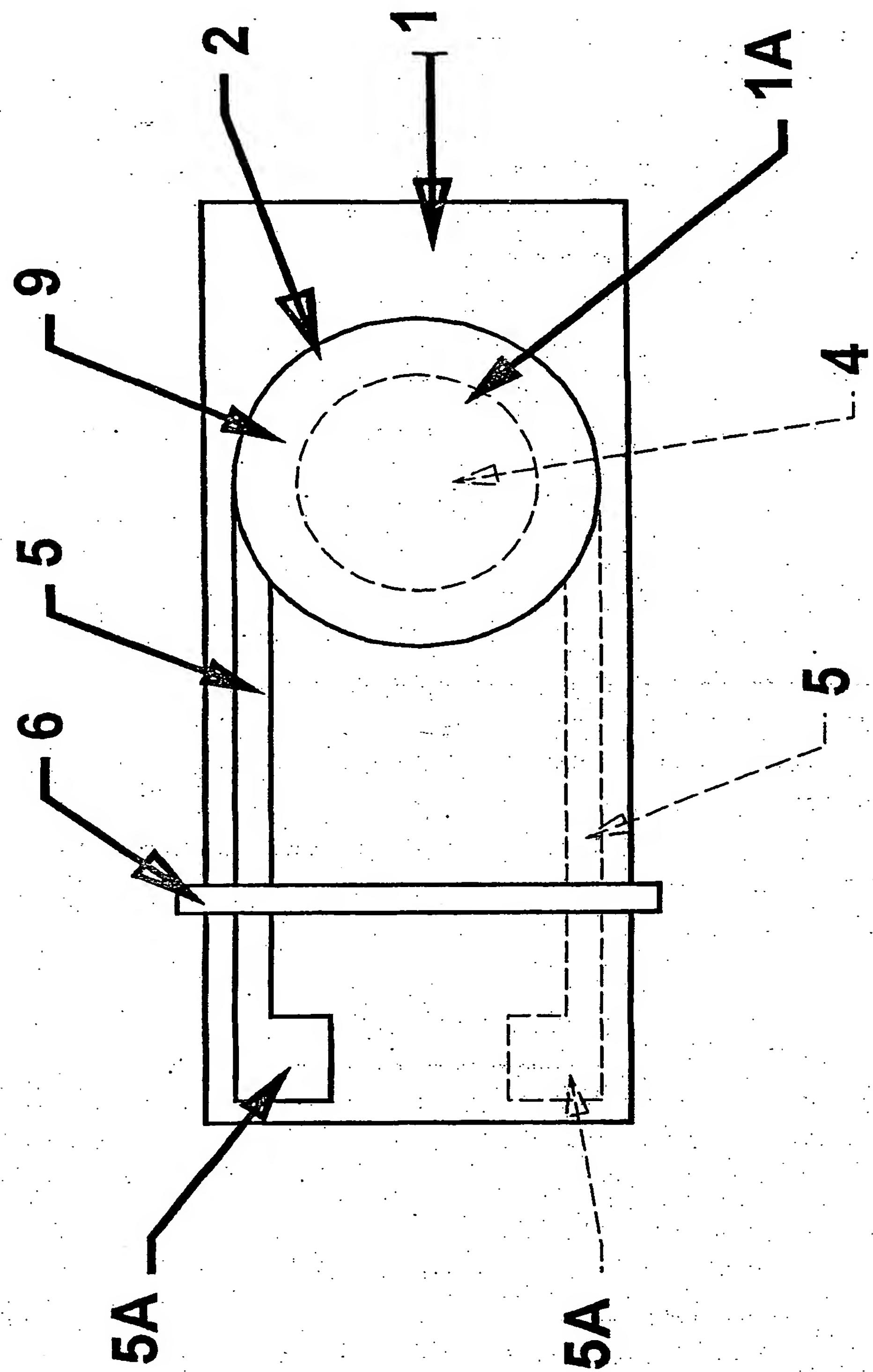


FIGURE 1A

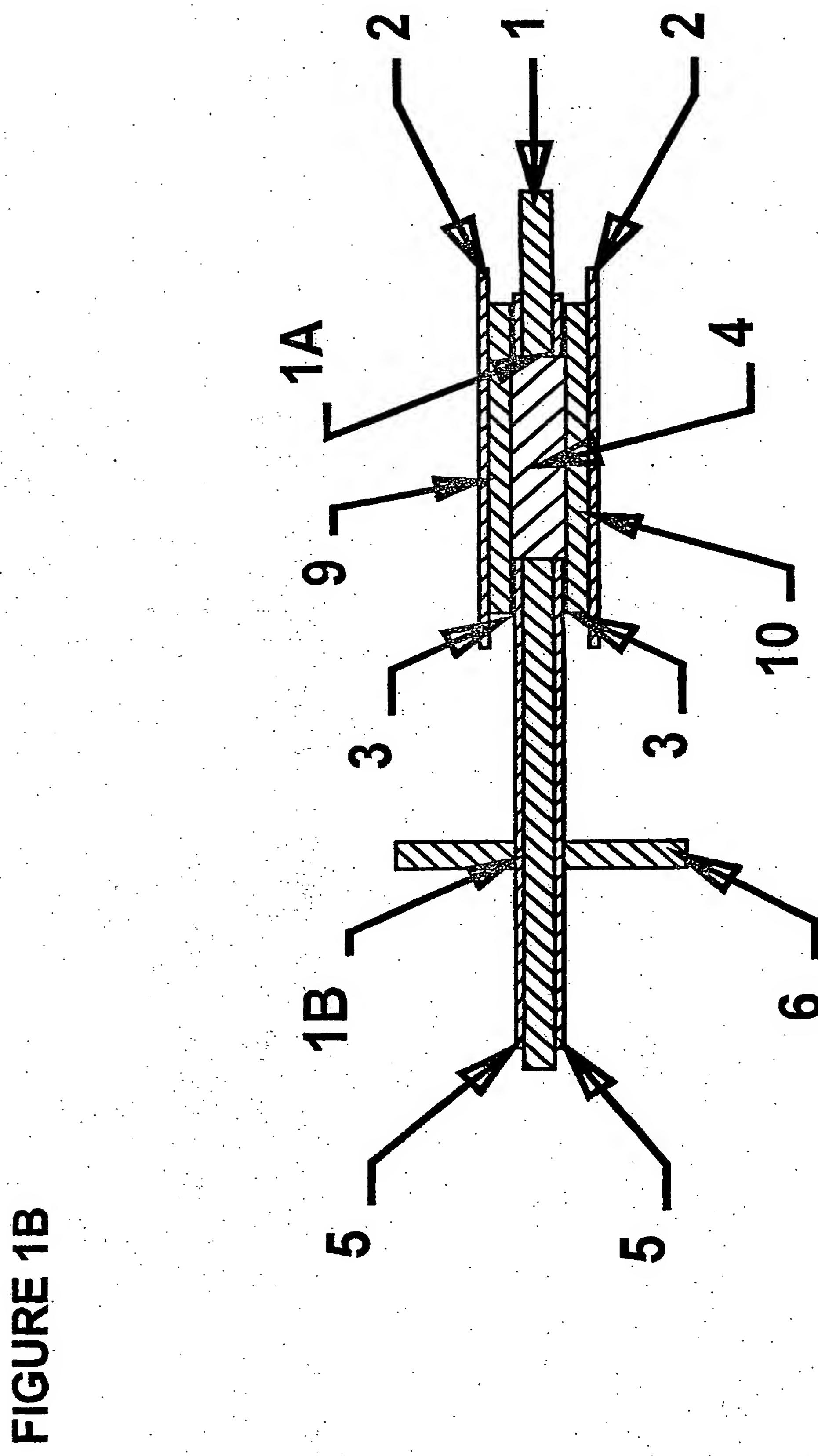


FIGURE 1B

SUBSTITUTE SHEET (RULE 26)

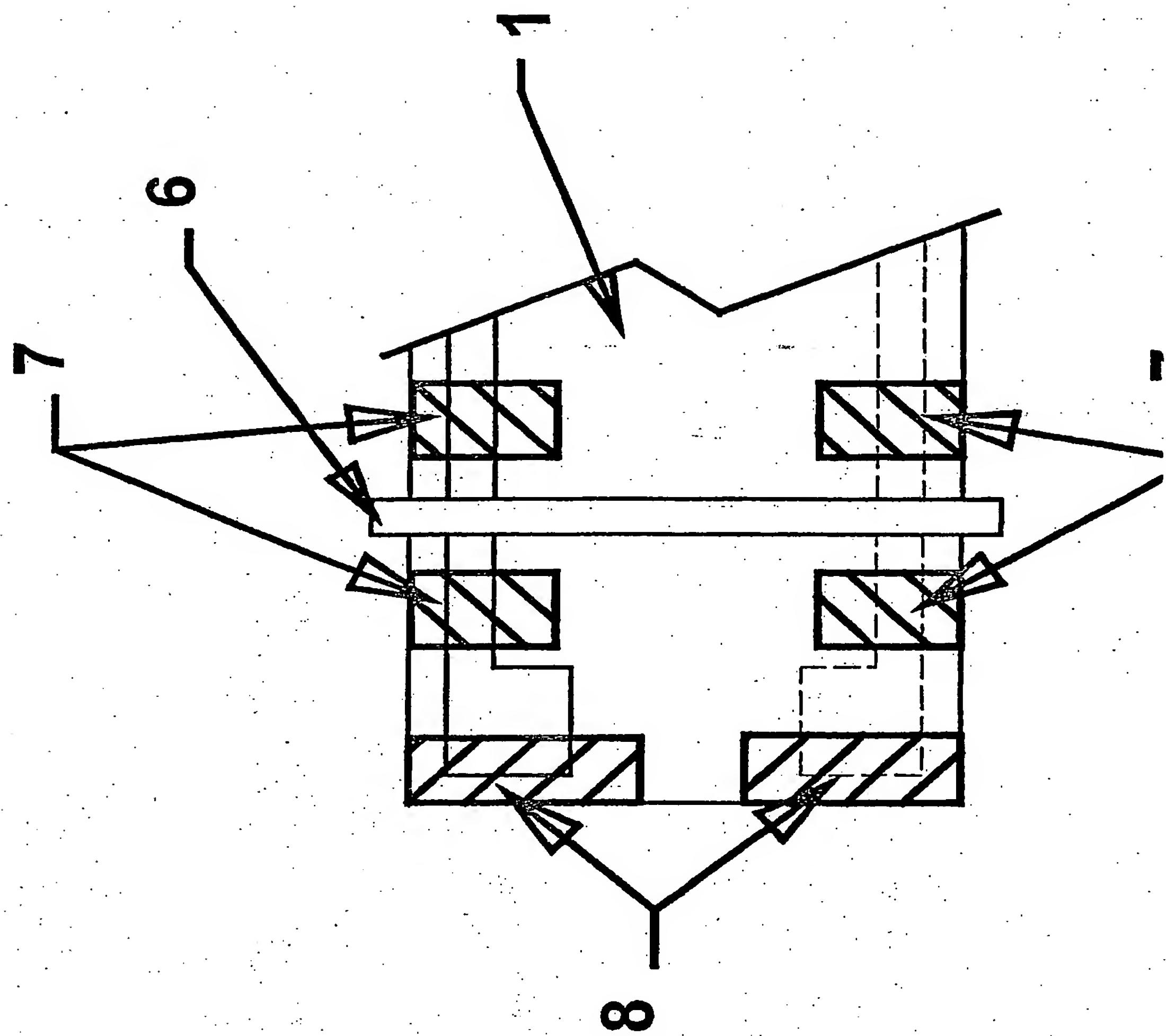


FIGURE 1C

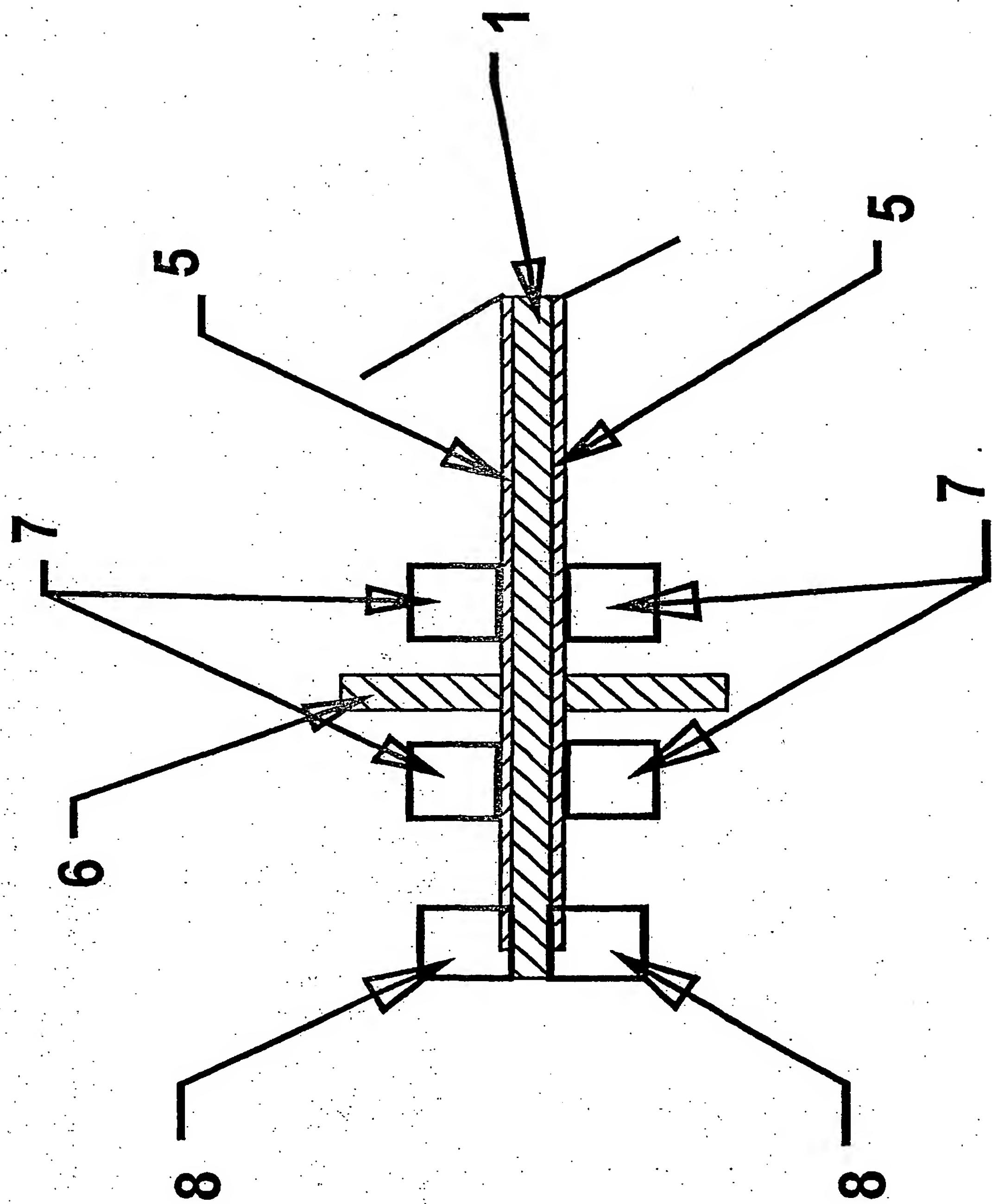


FIGURE 1D

SUBSTITUTE SHEET (RULE 26)

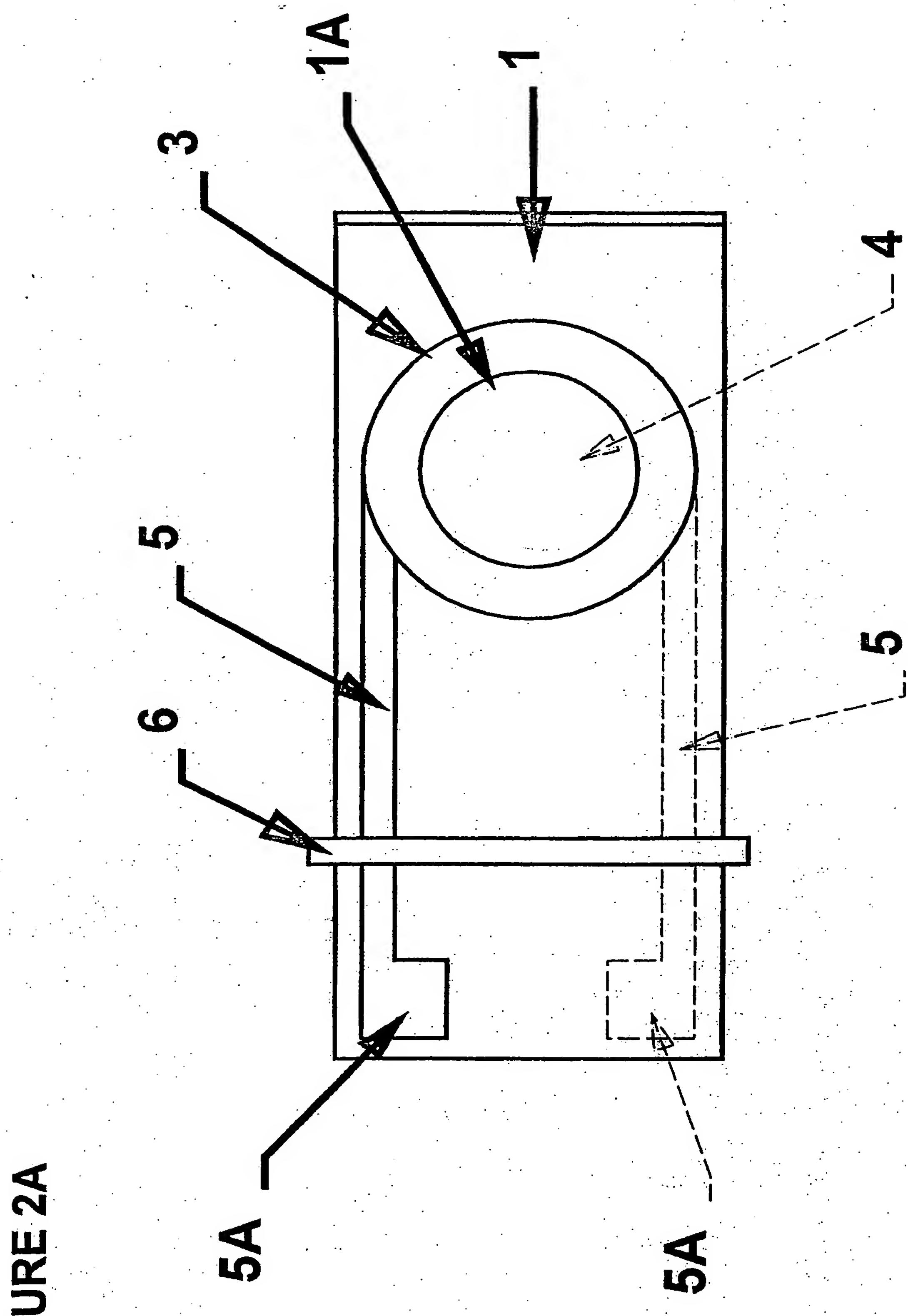
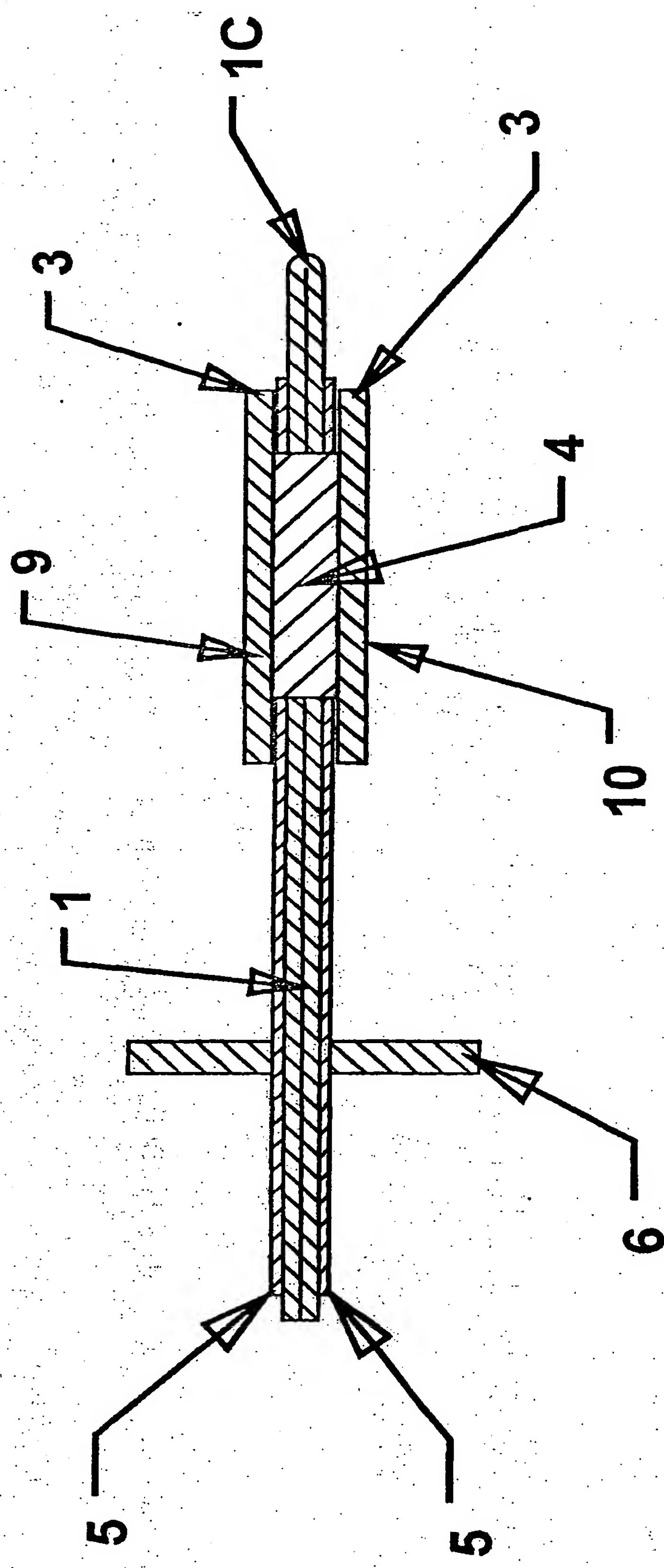


FIGURE 2A

FIGURE 2B**SUBSTITUTE SHEET (RULE 26)**

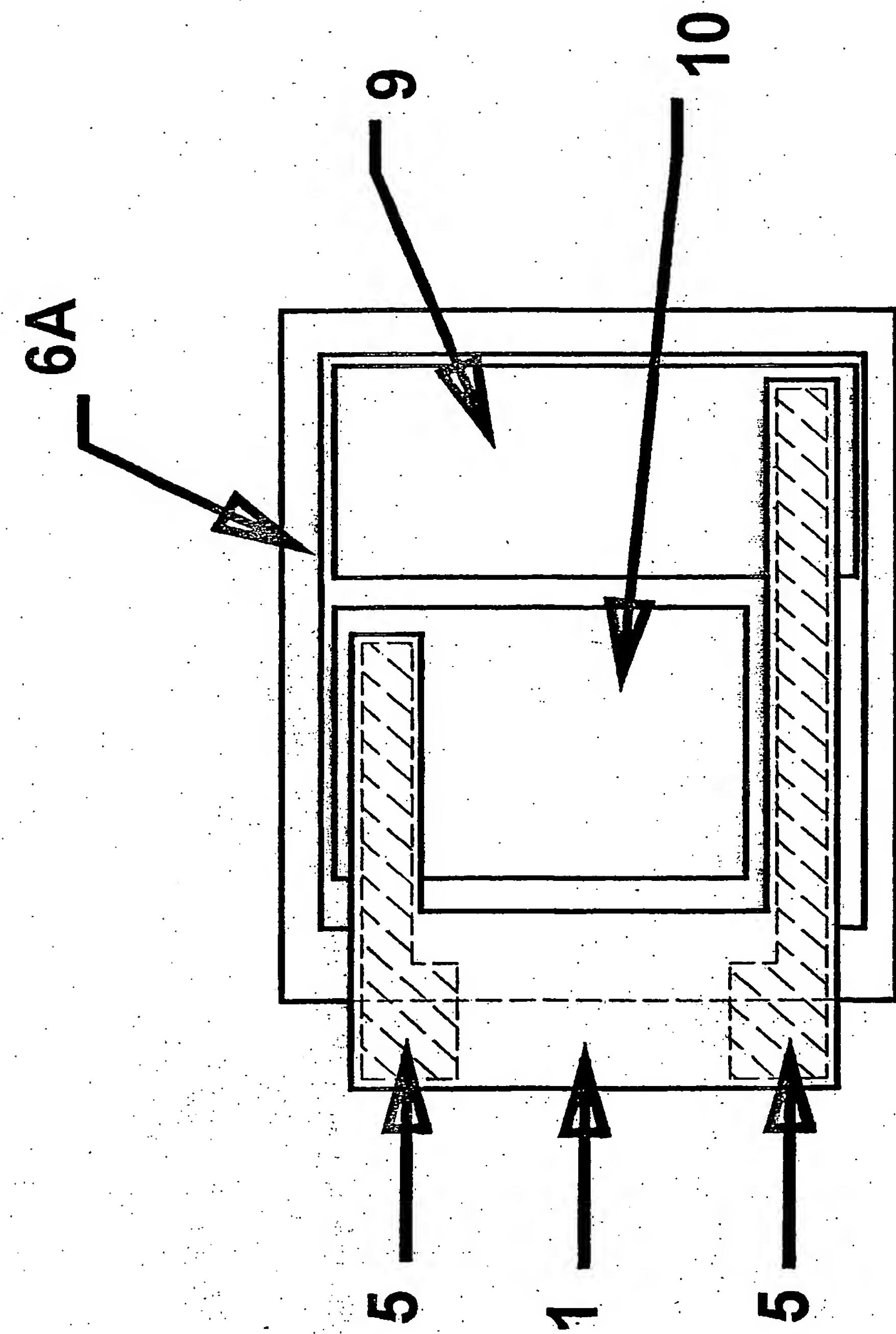


FIGURE 3A

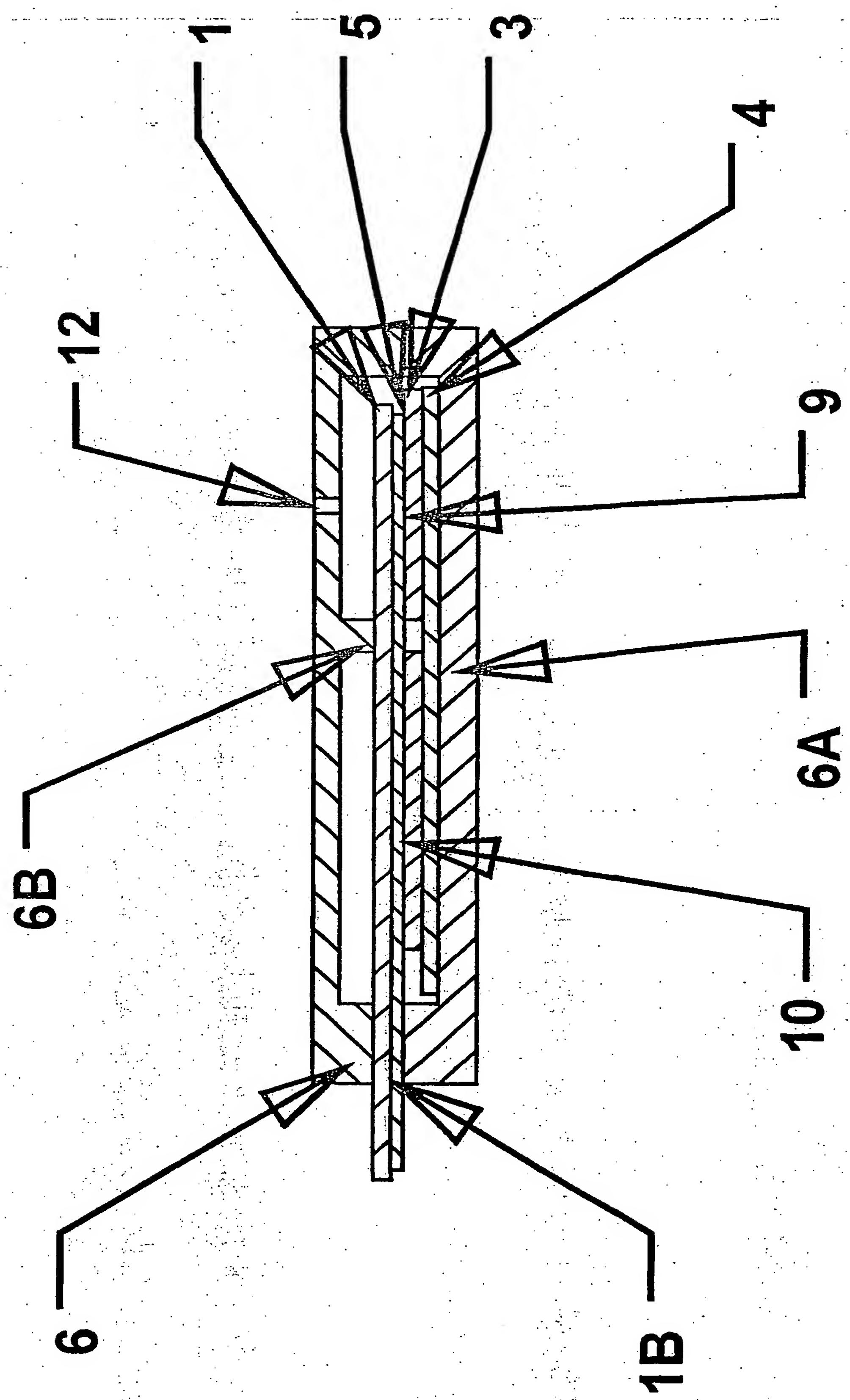


FIGURE 3B

SUBSTITUTE SHEET (RULE 26)

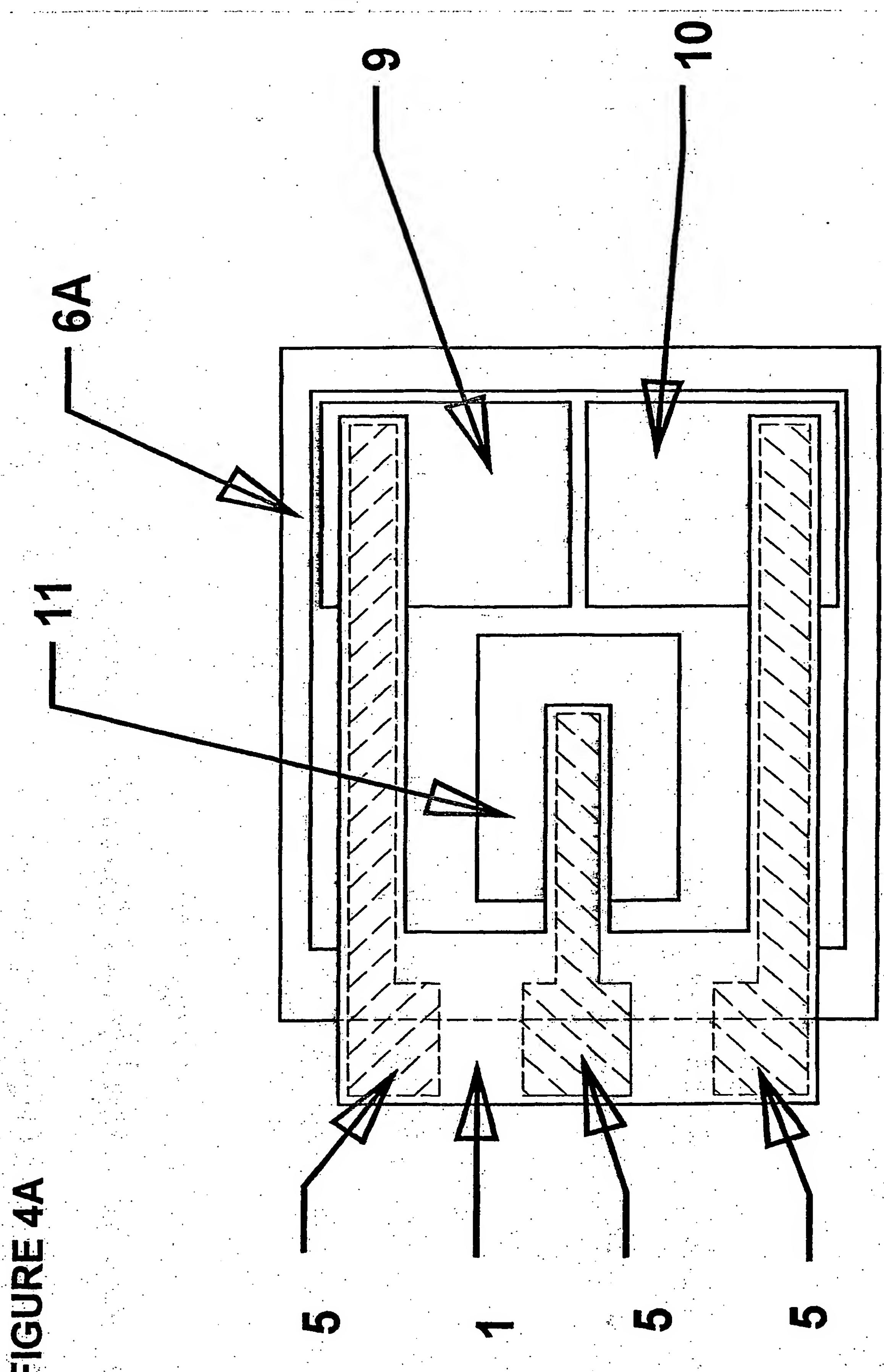


FIGURE 4A

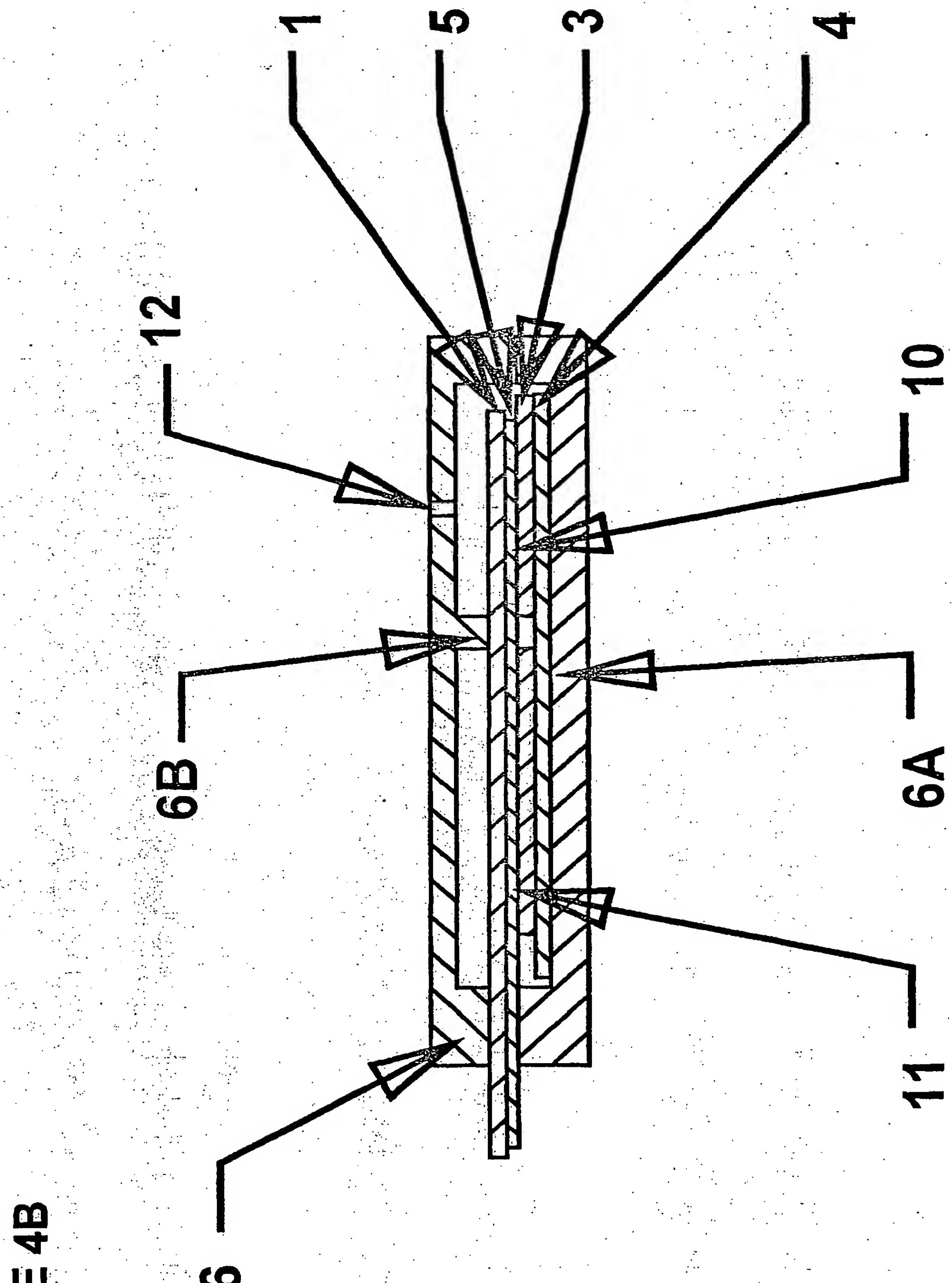


FIGURE 4B

SUBSTITUTE SHEET (RULE 26)

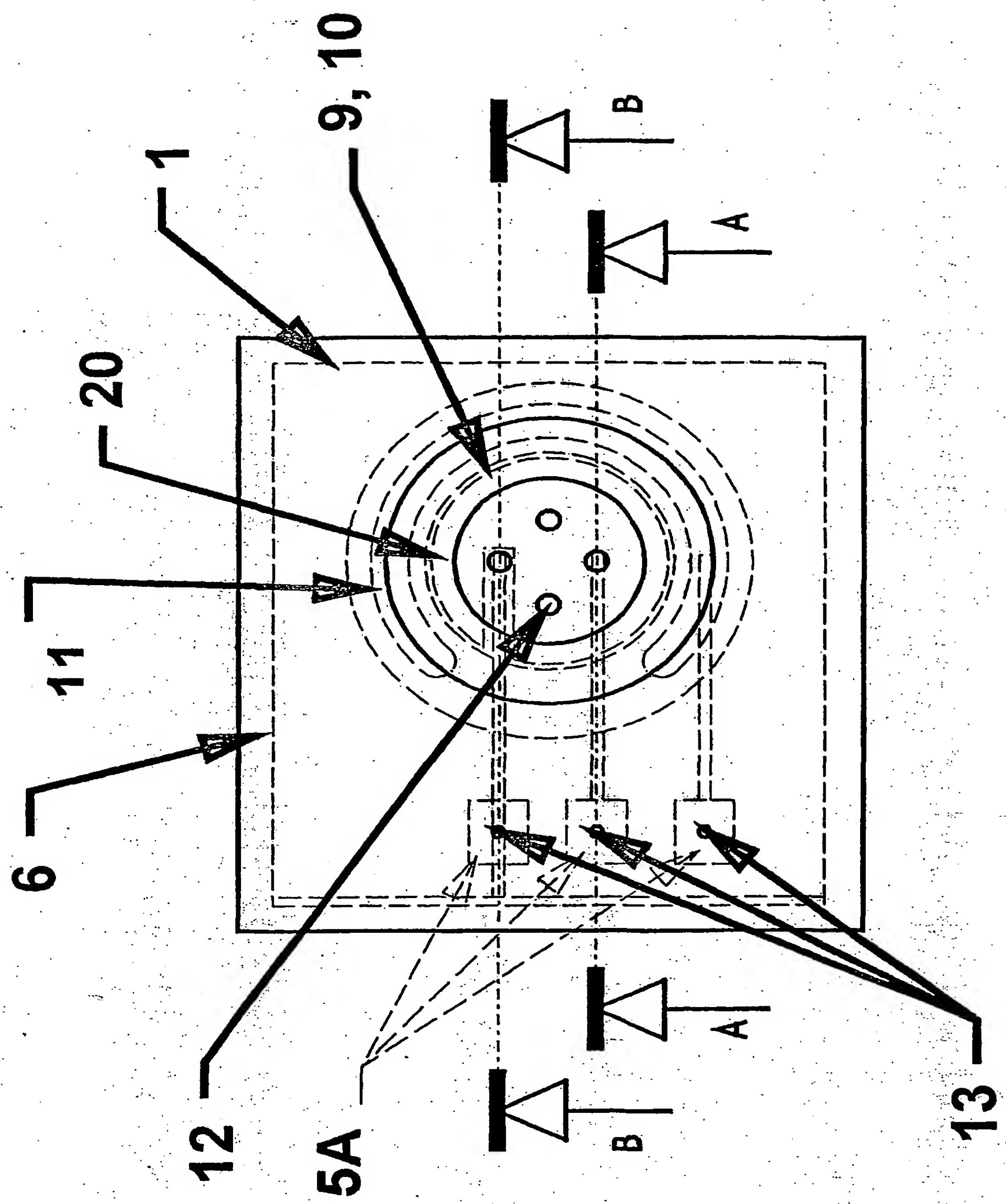
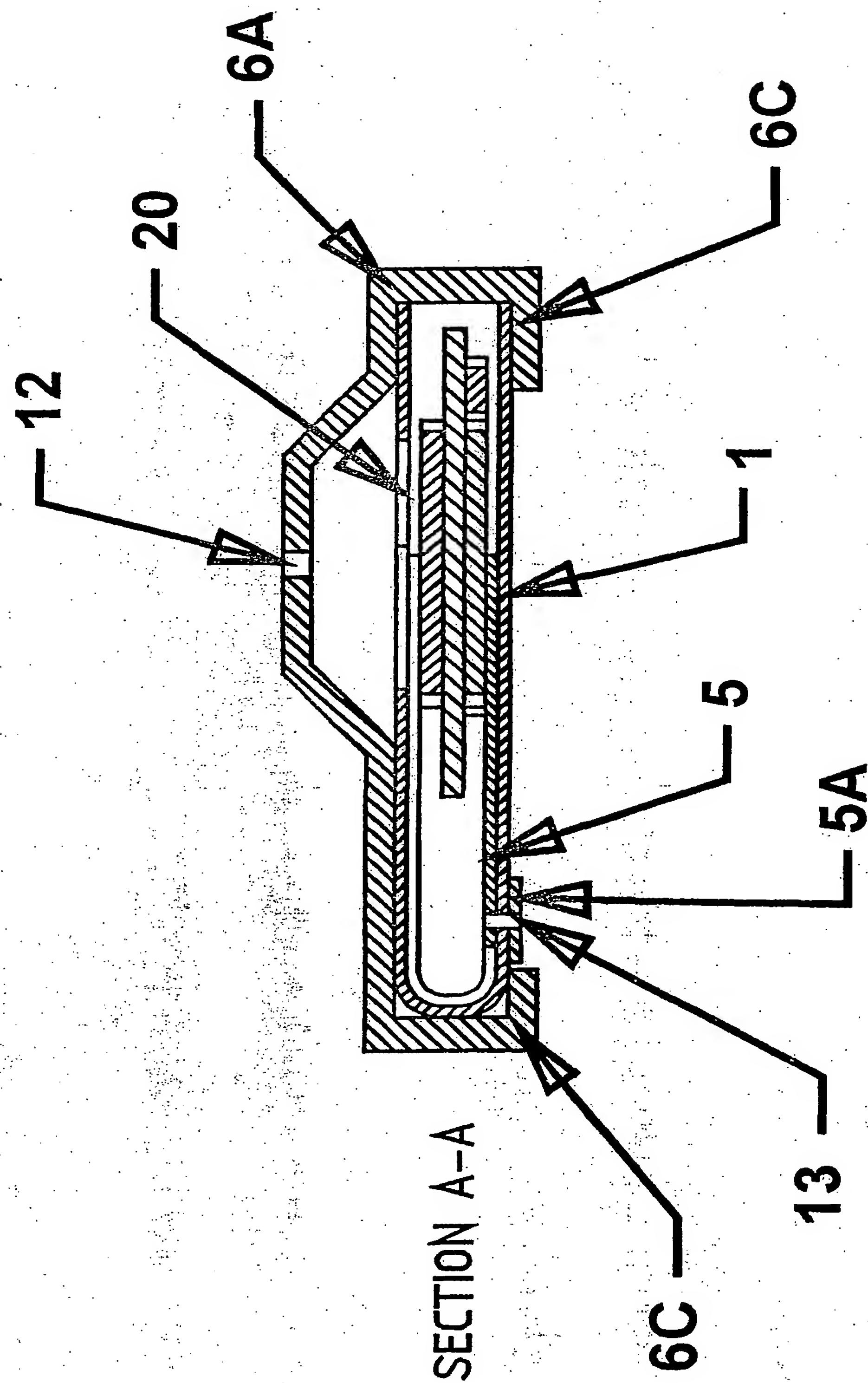


FIGURE 5A

FIGURE 5B

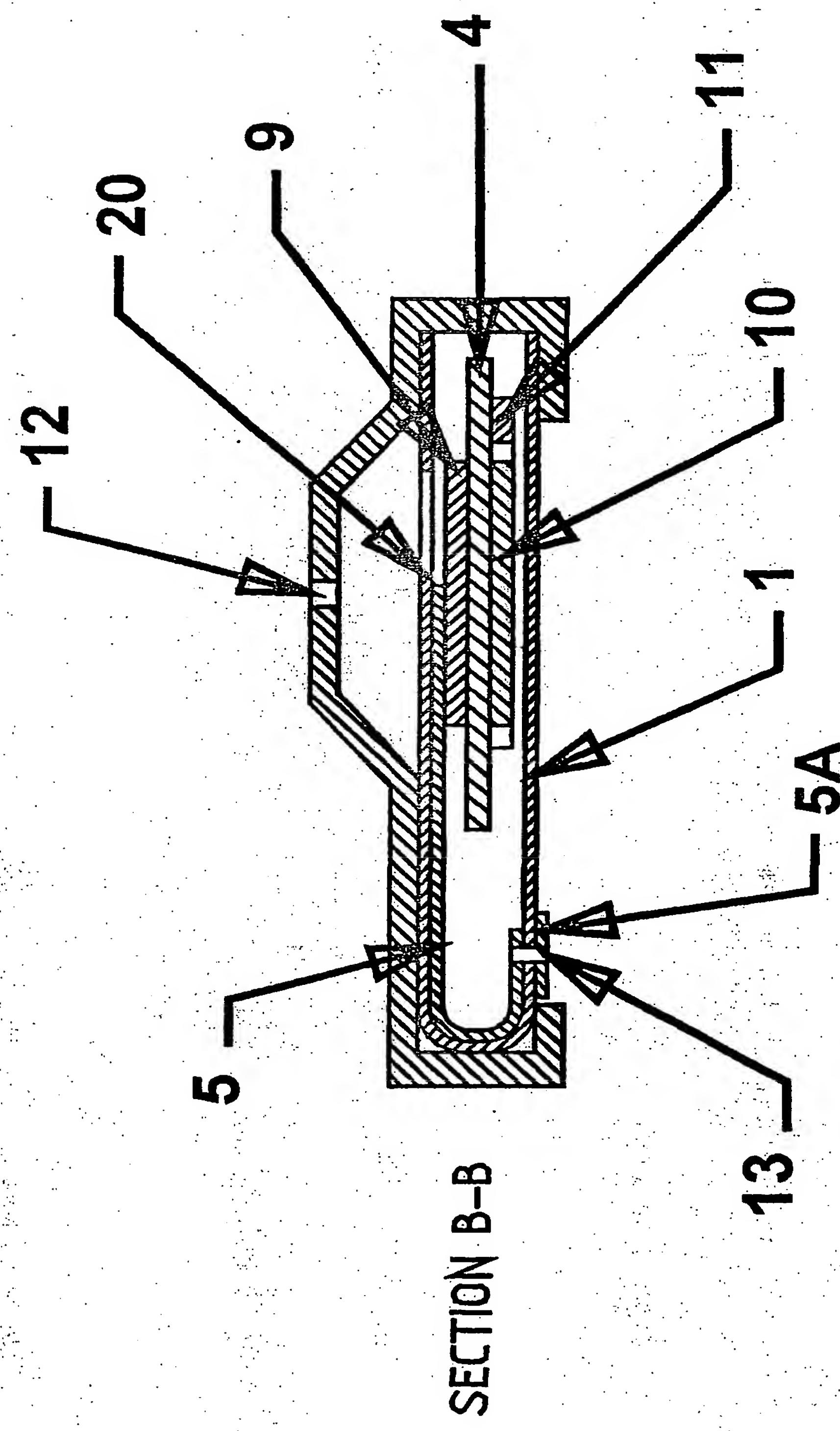
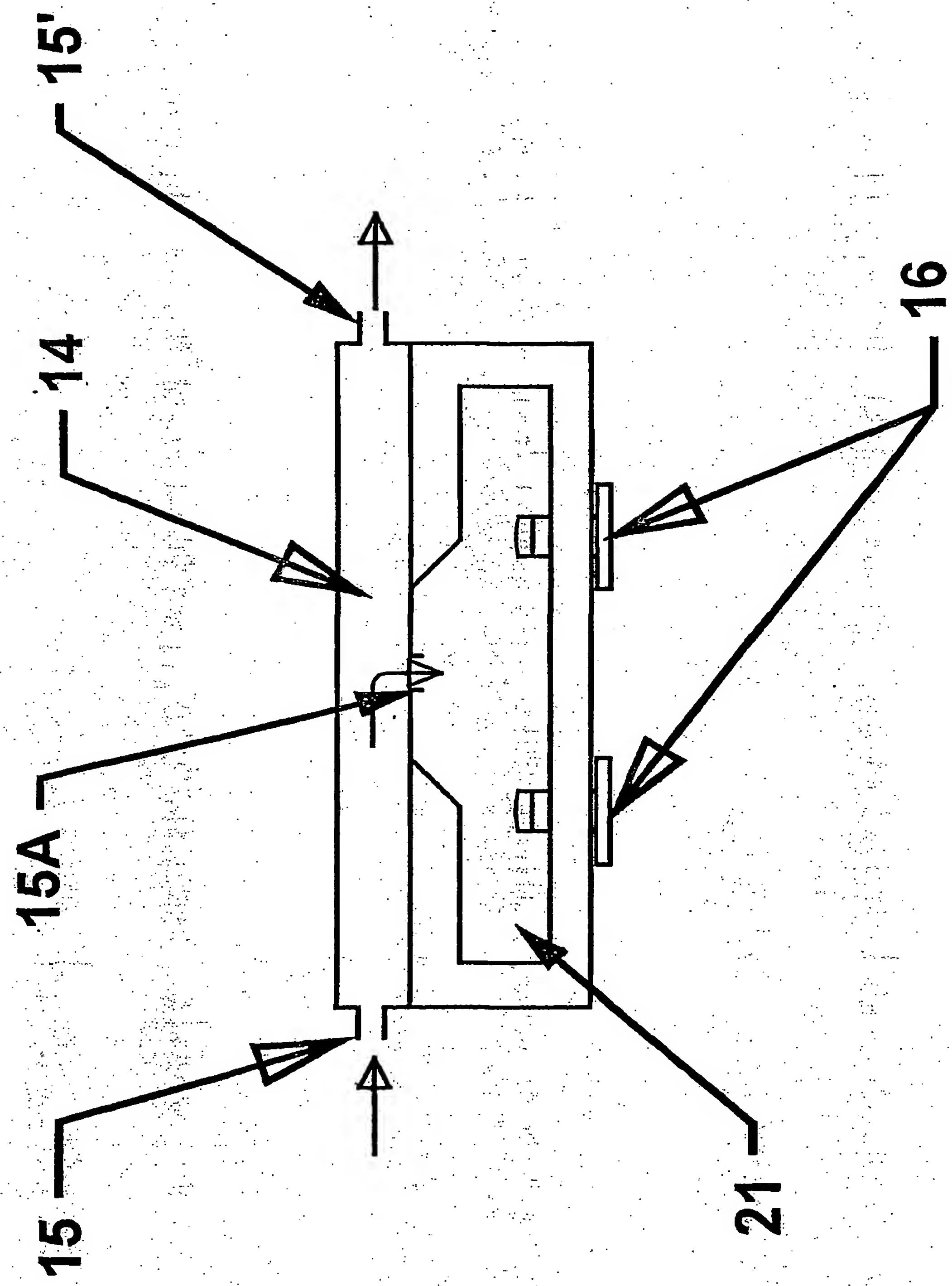


FIGURE 5C

FIGURE 6

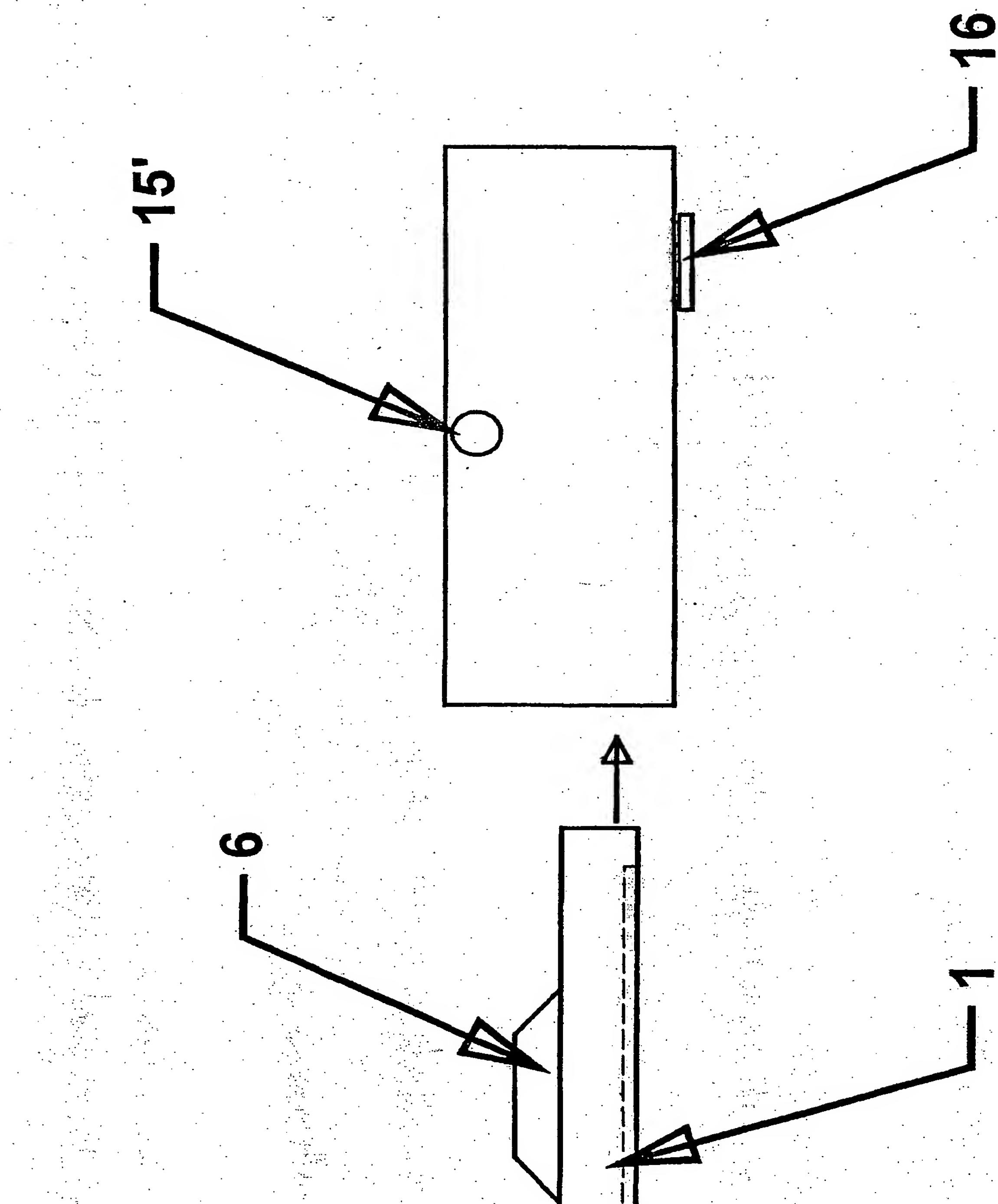


FIGURE 7

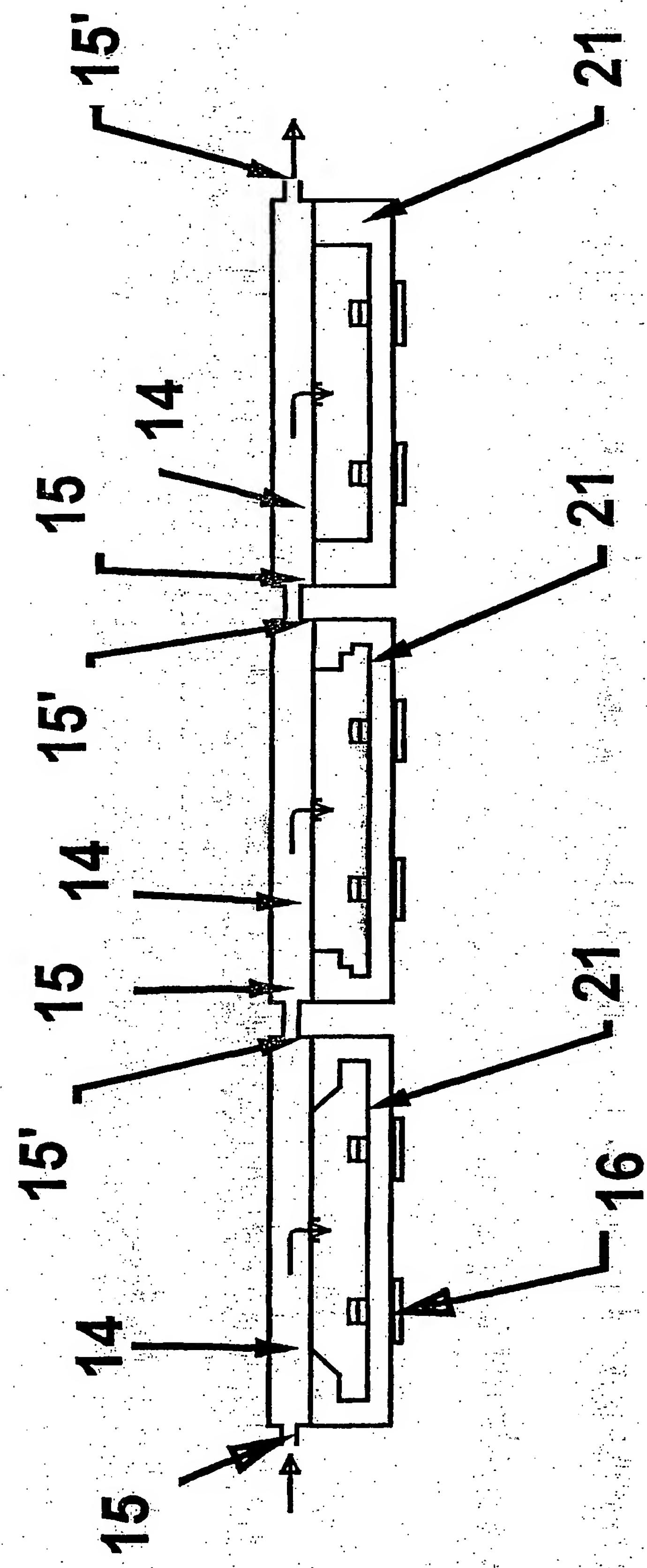
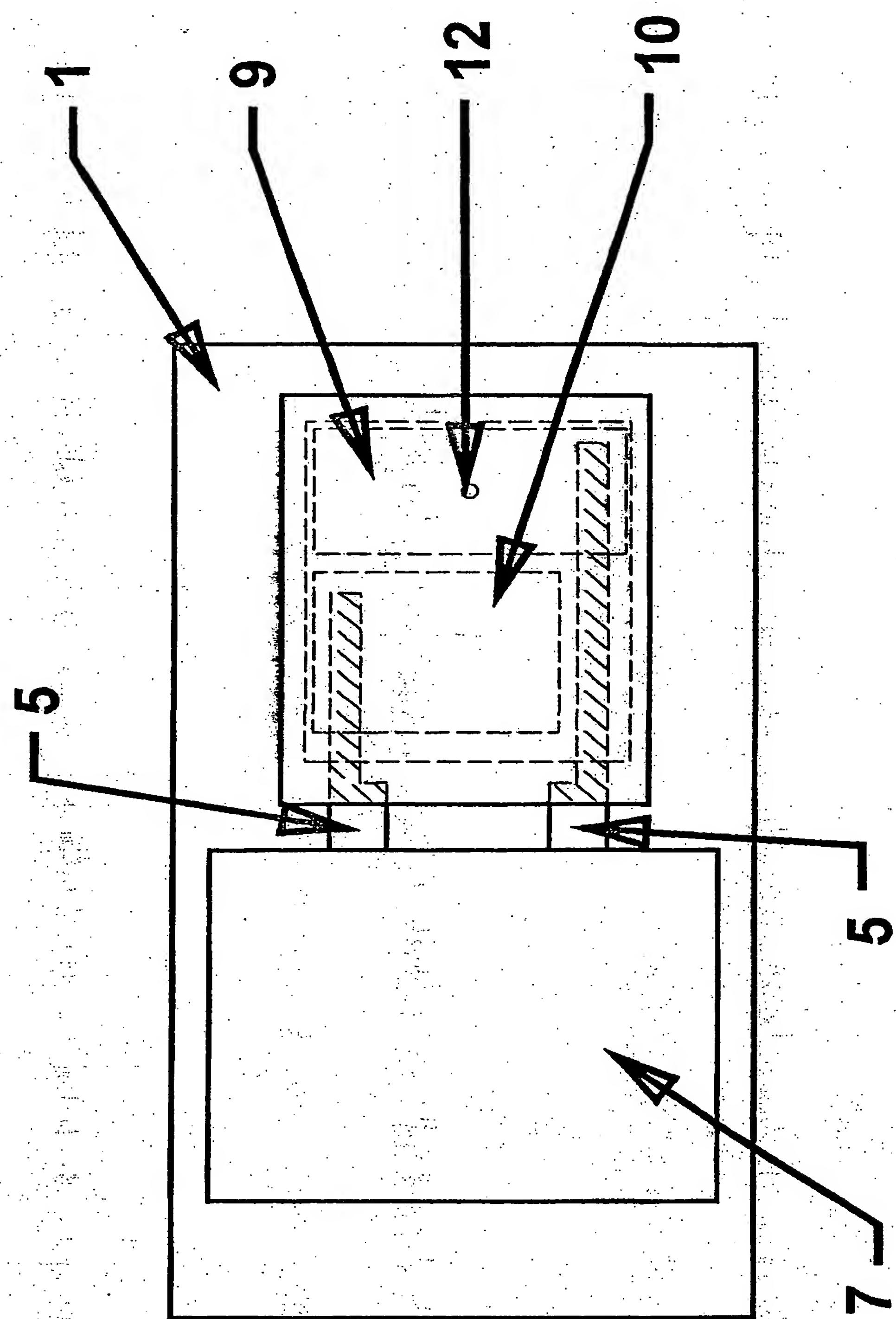
FIGURE 8**SUBSTITUTE SHEET (RULE 26)**

FIGURE 9A

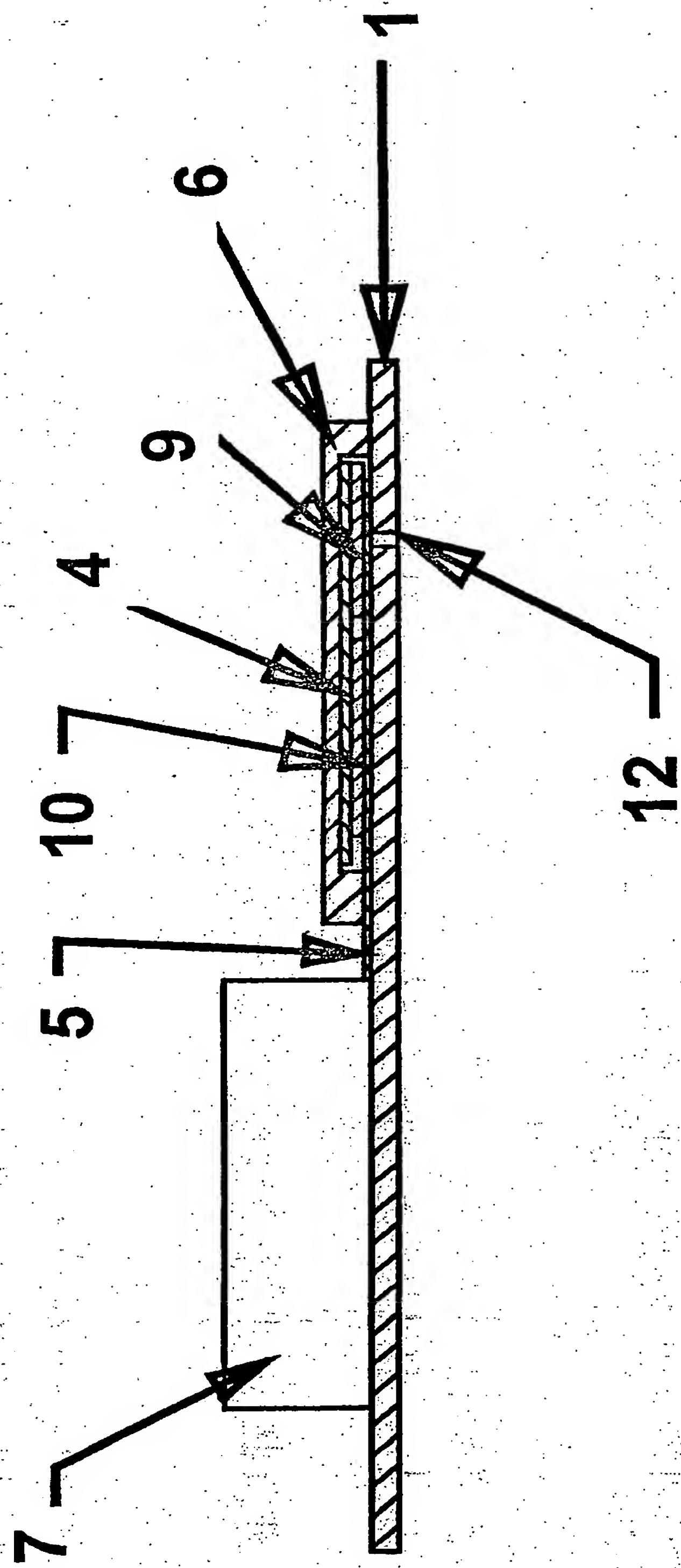


FIGURE 9B

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

**(19) World Intellectual Property Organization
International Bureau**



A standard linear barcode is positioned horizontally across the bottom of the page, consisting of vertical black bars of varying widths on a white background.

(43) International Publication Date
7 November 2002 (07.11.2002)

PCT

(10) International Publication Number
WO 02/088694 A3

(51) International Patent Classification⁷: G01N 27/407,
27/49

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/GB02/01984

(22) International Filing Date: 1 May 2002 (01.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(26) Publication Language: English

(30) Priority Data:
0110775.4 2 May 2001 (02.05.2001) GB

(71) **Applicant (for all designated States except US): CITY TECHNOLOGY LIMITED [GB/GB]; City Technology Centre, Walton Road, Portsmouth PO6 1SZ (GB).**

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): JONES, Martin, Geoffrey [GB/GB]; 56 Blenheim Gardens, Havant, Hampshire PO9 2PN (GB). COLLINS, Graham [GB/GB]; Warrens Cottage, Bridge Street, Wickham, Hants PO17 5JE (GB).

(74) Agent: **GILL JENNINGS & EVERY**; Broadgate House,
7 Eldon Street, London EC2M 7LH (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

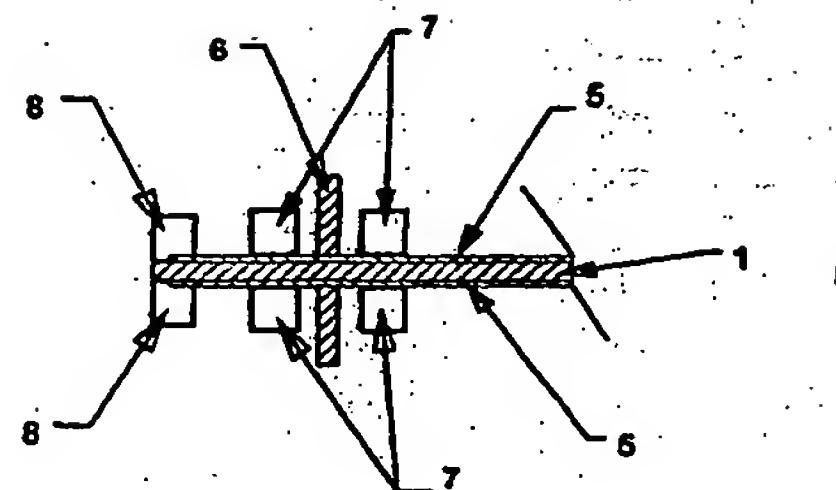
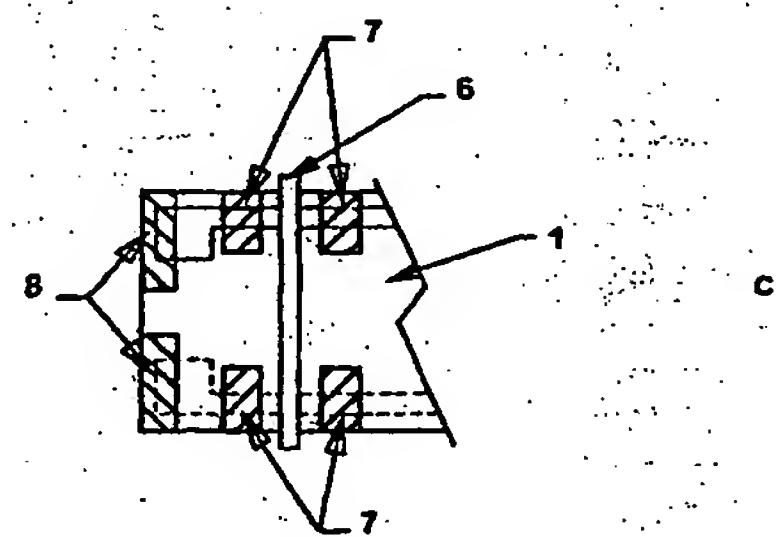
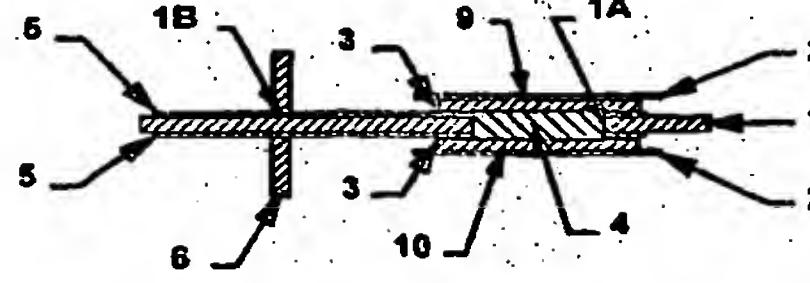
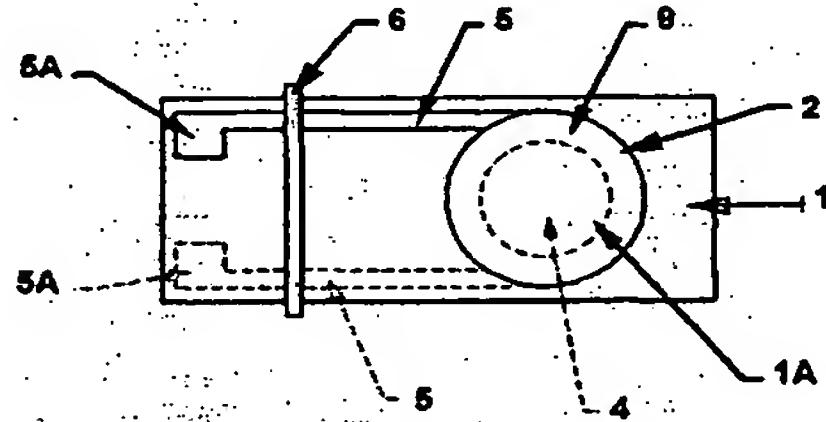
Published:

— with international search report

(88) Date of publication of the international search report:
27 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROCHEMICAL GAS SENSOR



(57) Abstract: An electrochemical gas sensor comprises sensing and counter electrodes (9, 10), current collectors (5) extending from each electrode, and a solid electrolyte (4) in contact with the electrodes, all supported on a common substrate (1) and located within a housing (6A) permitting gas access to the sensing electrode (9). The common substrate (1) projects from the housing to present portions of the current collectors for connection to other components.

WO 02/088694 A3

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 02/01984

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G01N27/407 G01N27/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 299 780 A (STANFORD RES INST INT) 18 January 1989 (1989-01-18) page 4, line 36 -page 5, line 52 page 7, line 25-31 page 8, line 22-30; figure 1	1-11,29, 30
A	---	12-22
Y	WO 96 24052 A (ATWOOD IND INC) 8 August 1996 (1996-08-08) page 9, line 1 -page 11, line 4	1-11,29, 30
A	WO 98 25138 A (DODGSON JOHN ROBERT ;AUSTEN MALCOLM TRAYTON (GB); CENTRAL RESEARCH) 11 June 1998 (1998-06-11) page 4, line 24-26 page 7, line 1-9 page 8, line 10-20	1
	---	-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

3 June 2003

Date of mailing of the international search report

11/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Brison, O

INTERNATIONAL SEARCH REPORT

Internat

Application No

PCT/GD 02/01984

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 326 481 A (CITY TECH) 23 December 1998 (1998-12-23) abstract page 1, line 3-17 page 4, line 8-13	1
A	WO 00 67011 A (HW ELECTROCHEM TECHNOLOGY PTE ;GE HAILIN (SG)) 9 November 2000 (2000-11-09) abstract; claims 1-5; figure 1	1,19
A	WO 96 27127 A (ANDROS INC) 6 September 1996 (1996-09-06) abstract; figures 1,2,4	1,23,24
A	US 5 215 643 A (AIZAWA KOICHI ET AL) 1 June 1993 (1993-06-01) column 4, line 3-46; figure 54	1

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 02/01984

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0299780	A	18-01-1989	US EP JP	4900405 A 0299780 A2 1088354 A		13-02-1990 18-01-1989 03-04-1989
WO 9624052	A	08-08-1996	US AU EP WO US	5573648 A 4971296 A 0807249 A1 9624052 A1 5650054 A		12-11-1996 21-08-1996 19-11-1997 08-08-1996 22-07-1997
WO 9825138	A	11-06-1998	CN EP WO JP KR TW US	1244257 A 0943090 A1 9825138 A1 2001505998 T 2000057438 A 396655 B 6376124 B1		09-02-2000 22-09-1999 11-06-1998 08-05-2001 15-09-2000 01-07-2000 23-04-2002
GB 2326481	A	23-12-1998	NONE			
WO 0067011	A	09-11-2000	WO	0067011 A1		09-11-2000
WO 9627127	A	06-09-1996	US CA EP JP WO	5582797 A 2212697 A1 0812417 A1 11501098 T 9627127 A1		10-12-1996 06-09-1996 17-12-1997 26-01-1999 06-09-1996
US 5215643	A	01-06-1993	JP JP JP JP JP JP JP JP JP CH DE DE GB WO	1216252 A 2669527 B2 1216256 A 1216257 A 2501856 B2 1289011 A 2036345 A 2607631 B2 678660 A5 3990187 C2 3990187 T0 2228327 A ,B 8908249 A1		30-08-1989 29-10-1997 30-08-1989 30-08-1989 29-05-1996 21-11-1989 06-02-1990 07-05-1997 15-10-1991 25-11-1993 15-03-1990 22-08-1990 08-09-1989

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



BLACK BORDERS

- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.